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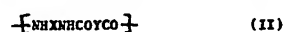
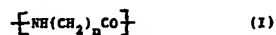
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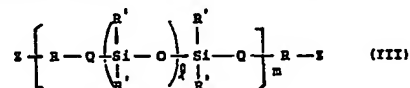
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## (54) Polyamide/polysiloxane copolymers

(57) There is disclosed a polyamide-polysiloxane copolymer. The polyamide constituent has repeating units of formulae (I) and/or (II):



wherein n is an integer from 5 to 11, X is a C<sub>6</sub> - C<sub>12</sub> alkylene radical and Y is a C<sub>4</sub> - C<sub>10</sub> alkylene radical, and has amino groups or carboxyl groups at both terminals. The polyorganosiloxane constituent has the formula (III):

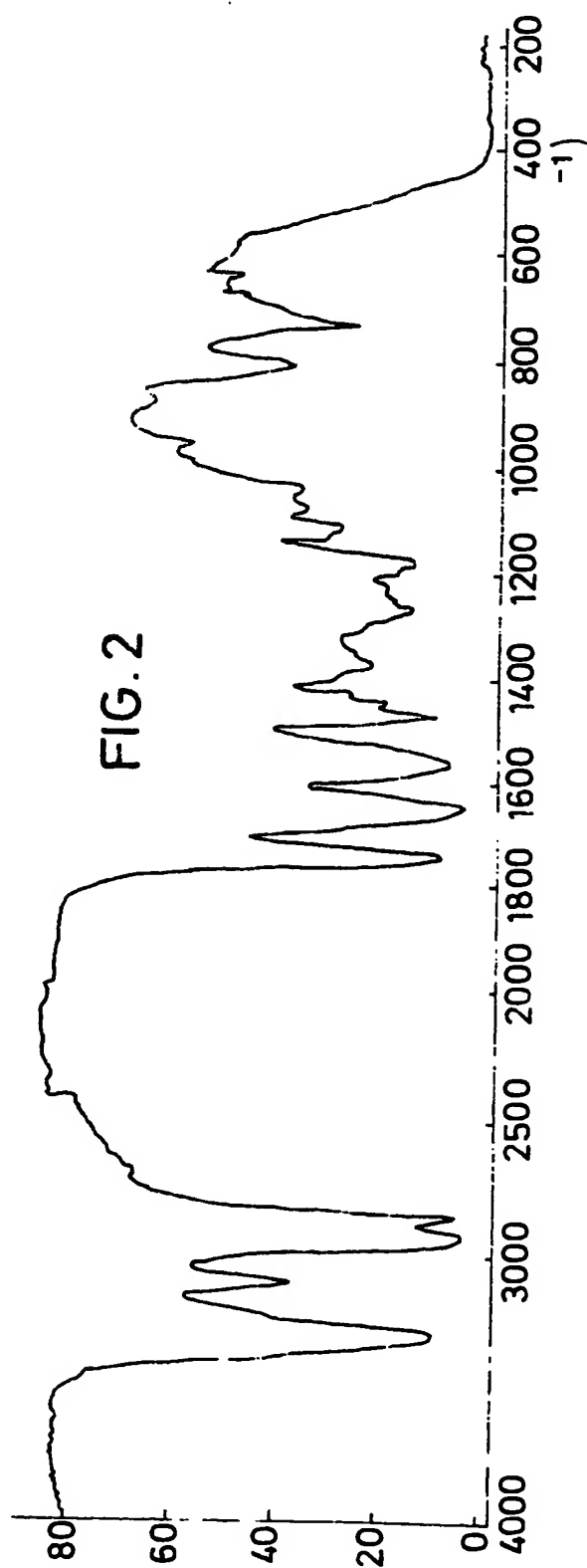
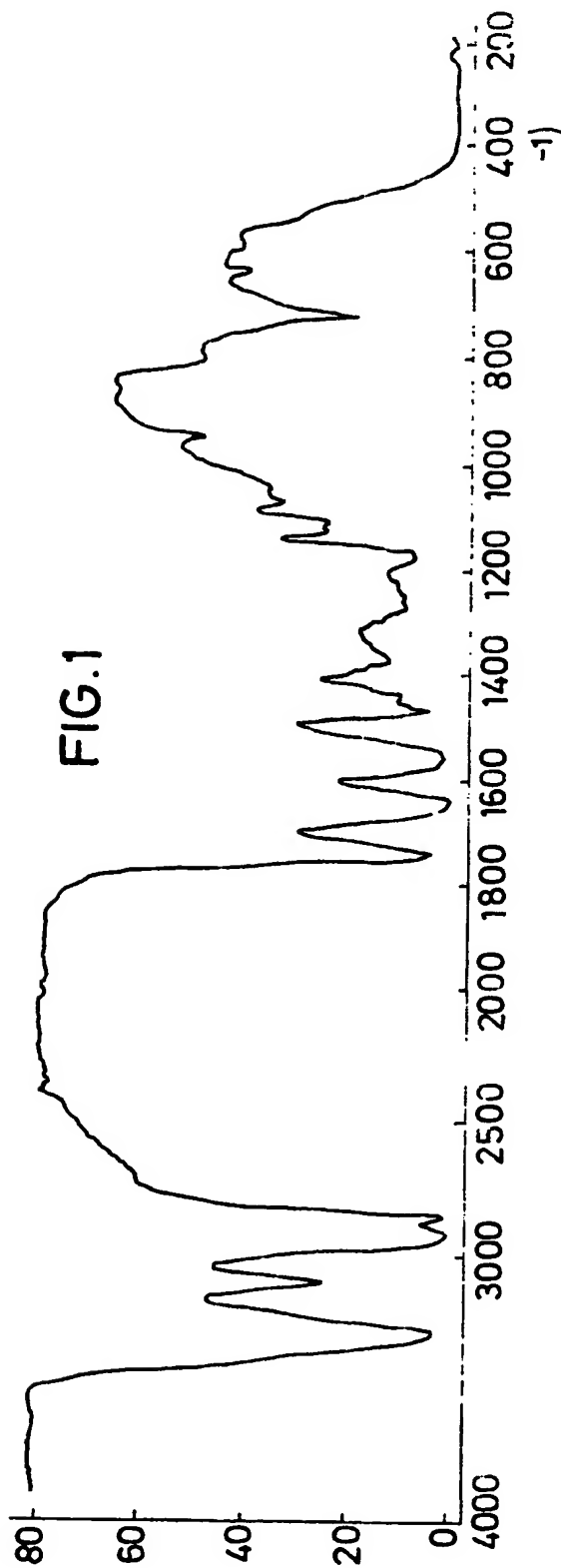


wherein l is an integer from 2 to 50, m is an integer from 1 to 6, Q is an oxygen atom or a direct bond, R' is a hydrogen atom, a methyl group or a phenyl group, R is a divalent organic radical and Z is a hydroxyl group an amino group or a carboxyl group. The constituents are polymerized by amide linkages or ester linkages to give a straight chain copolymer having a J-value of 10—600 ml/g.

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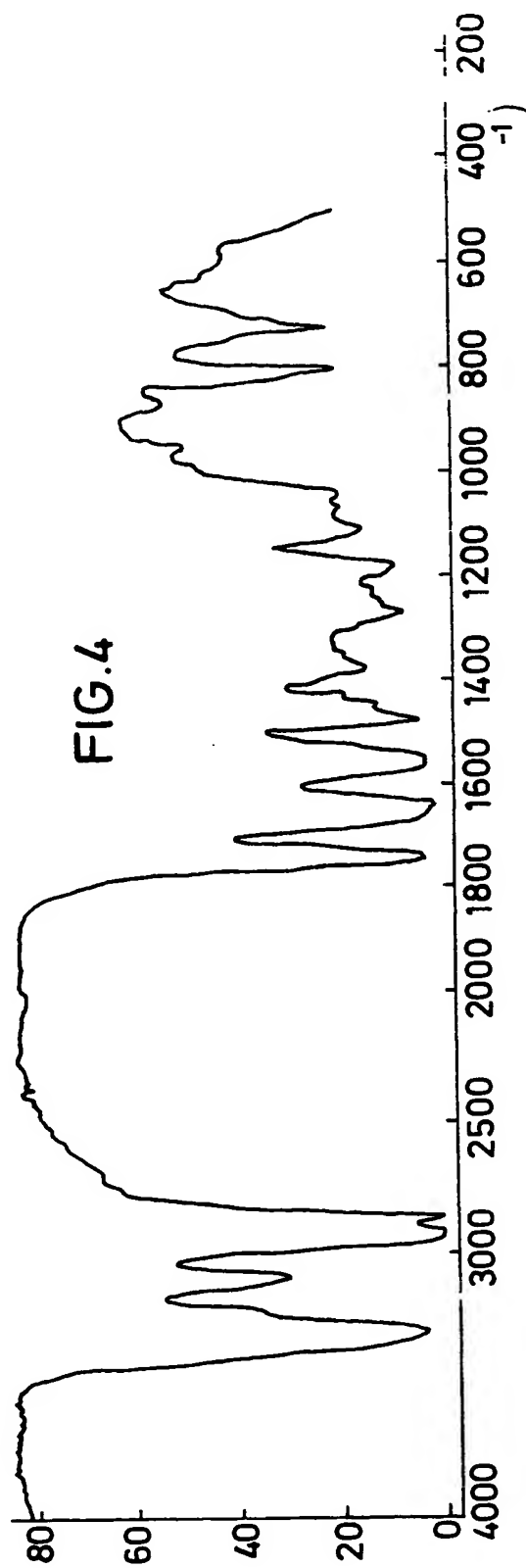
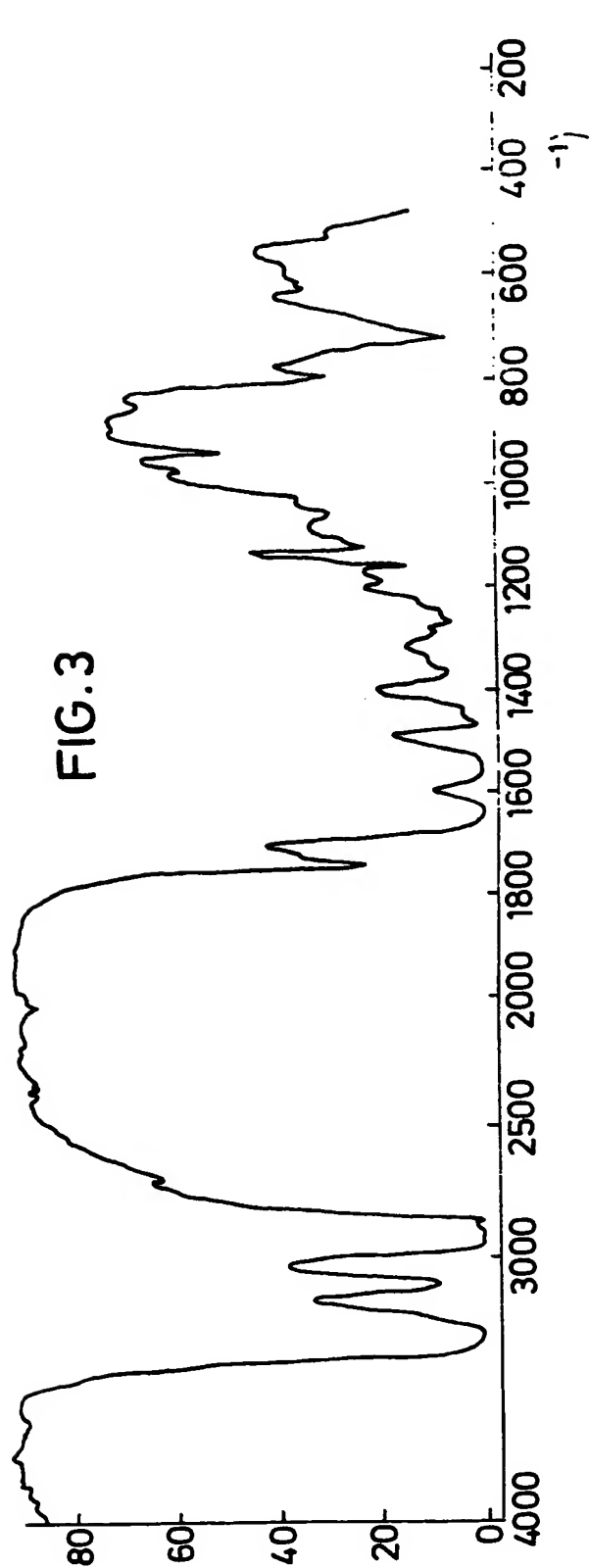
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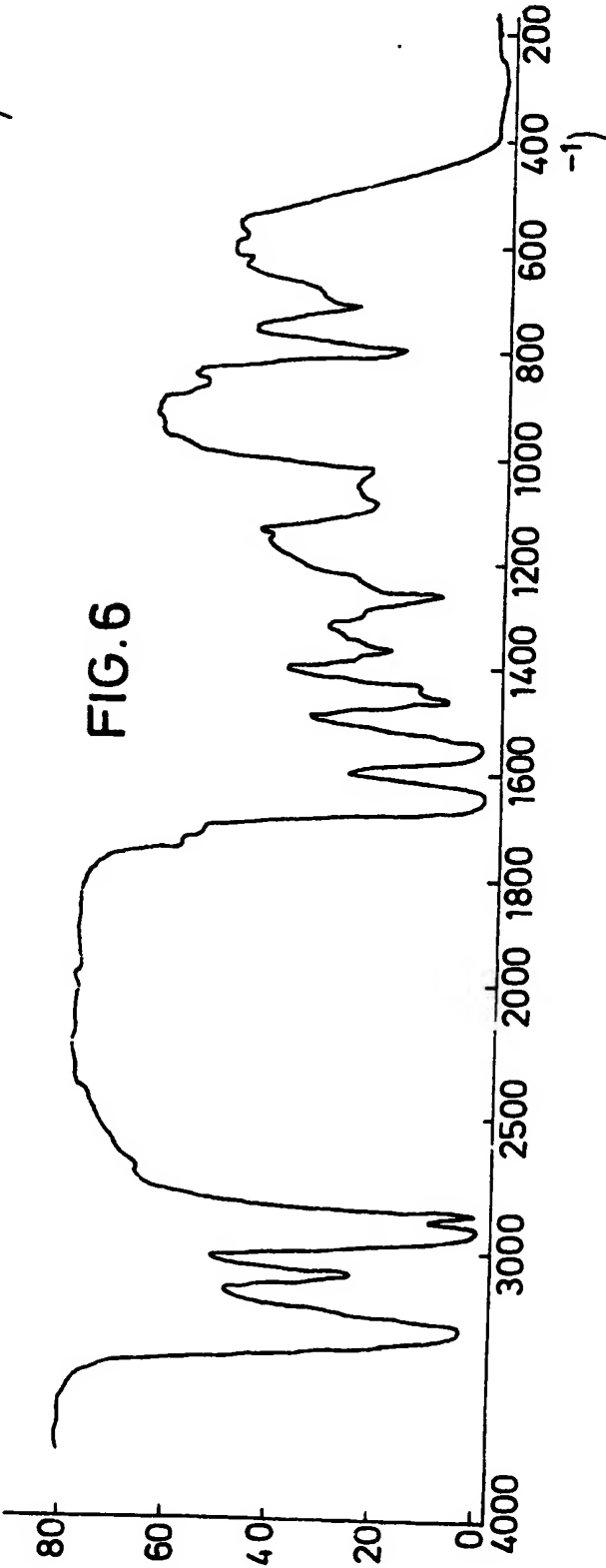
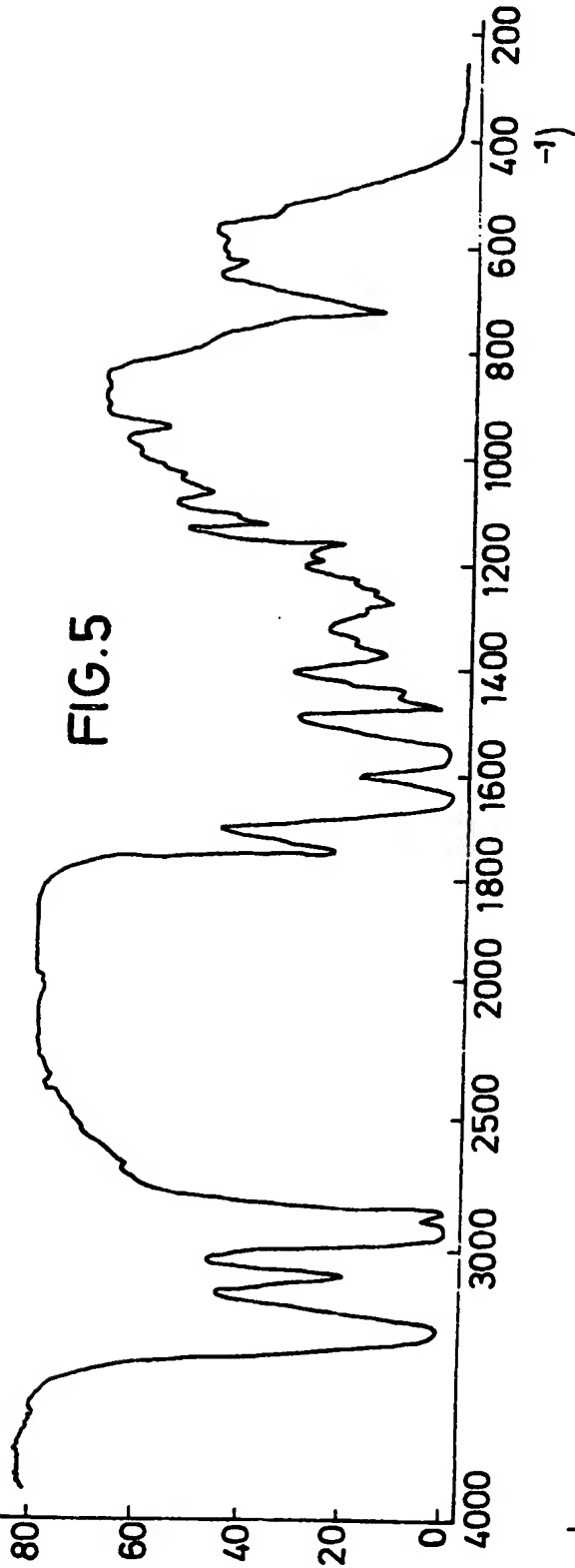
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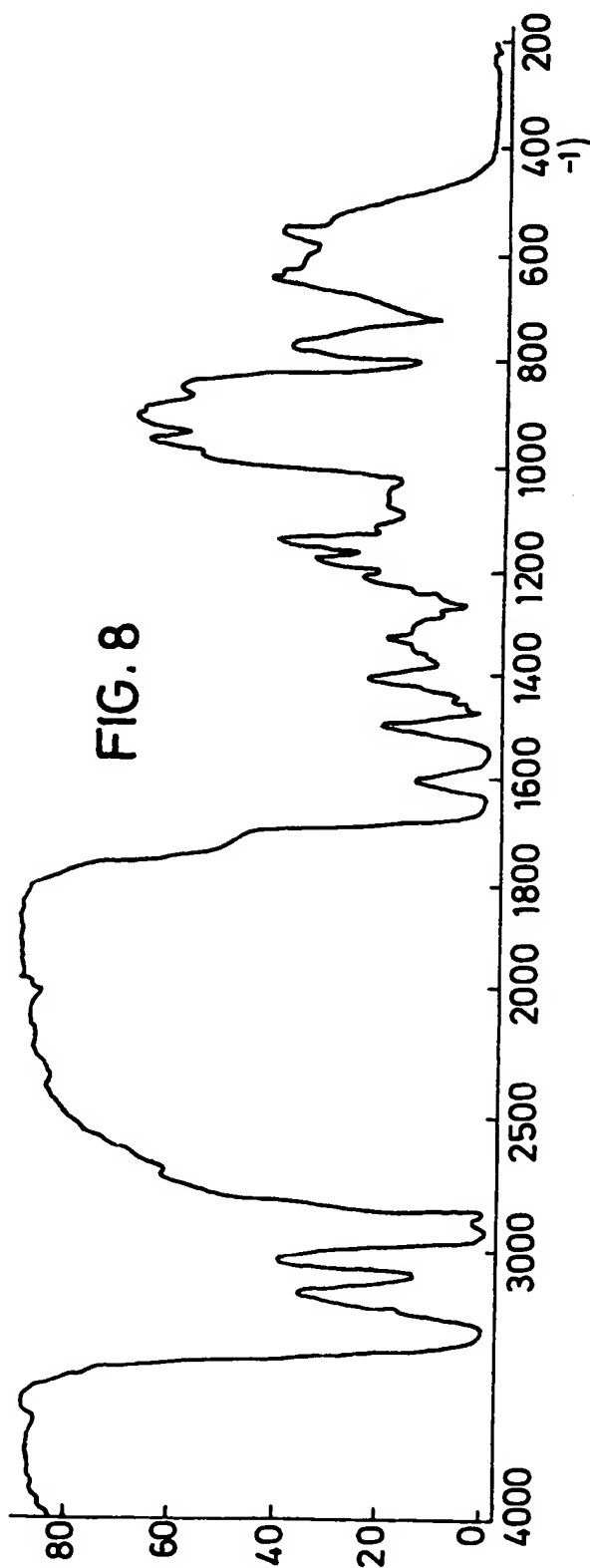
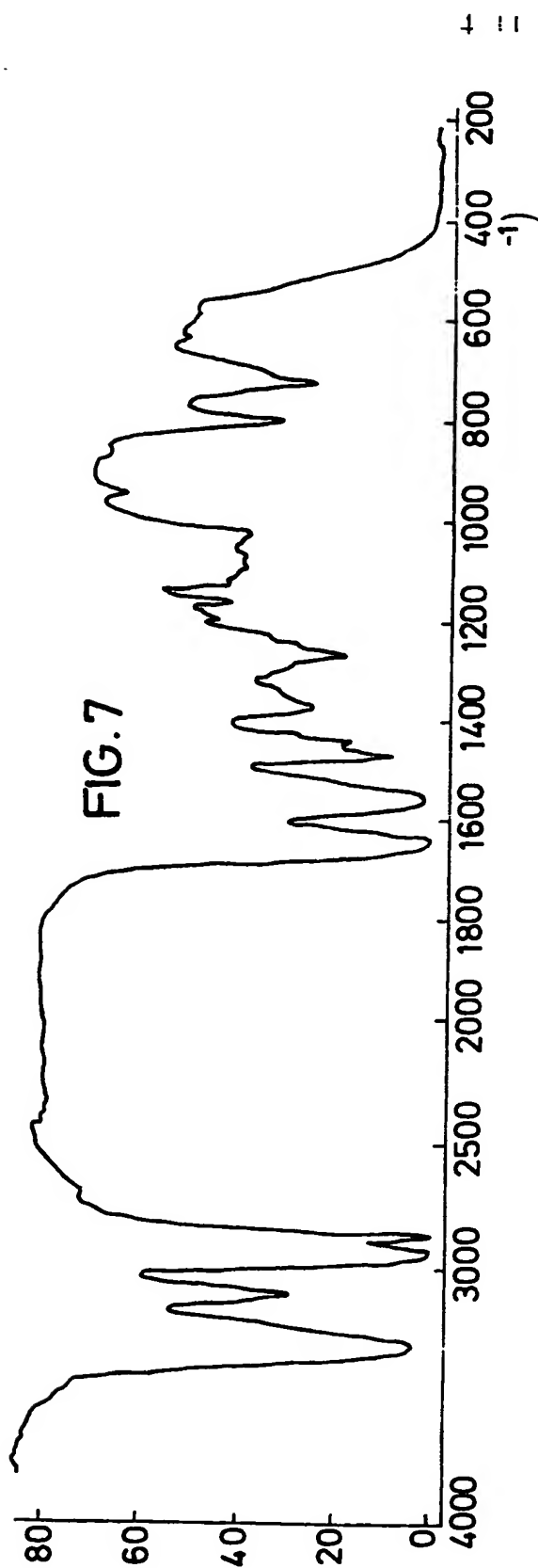


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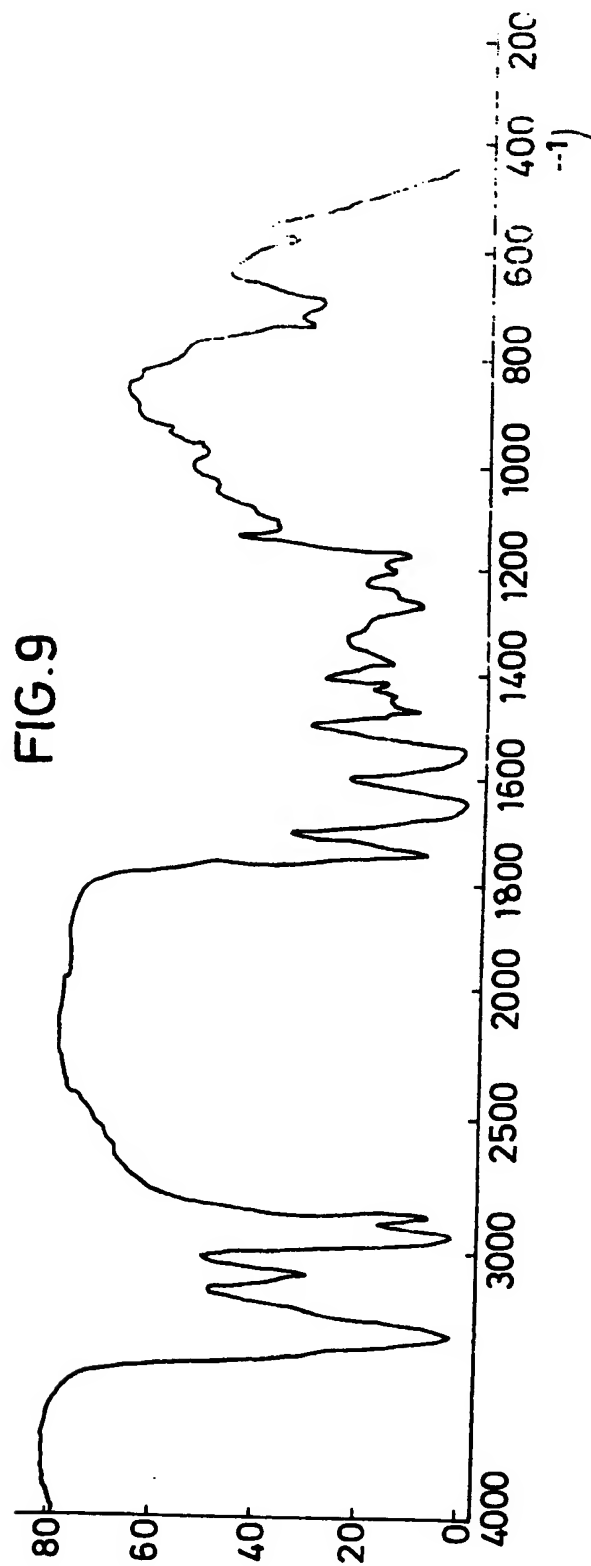


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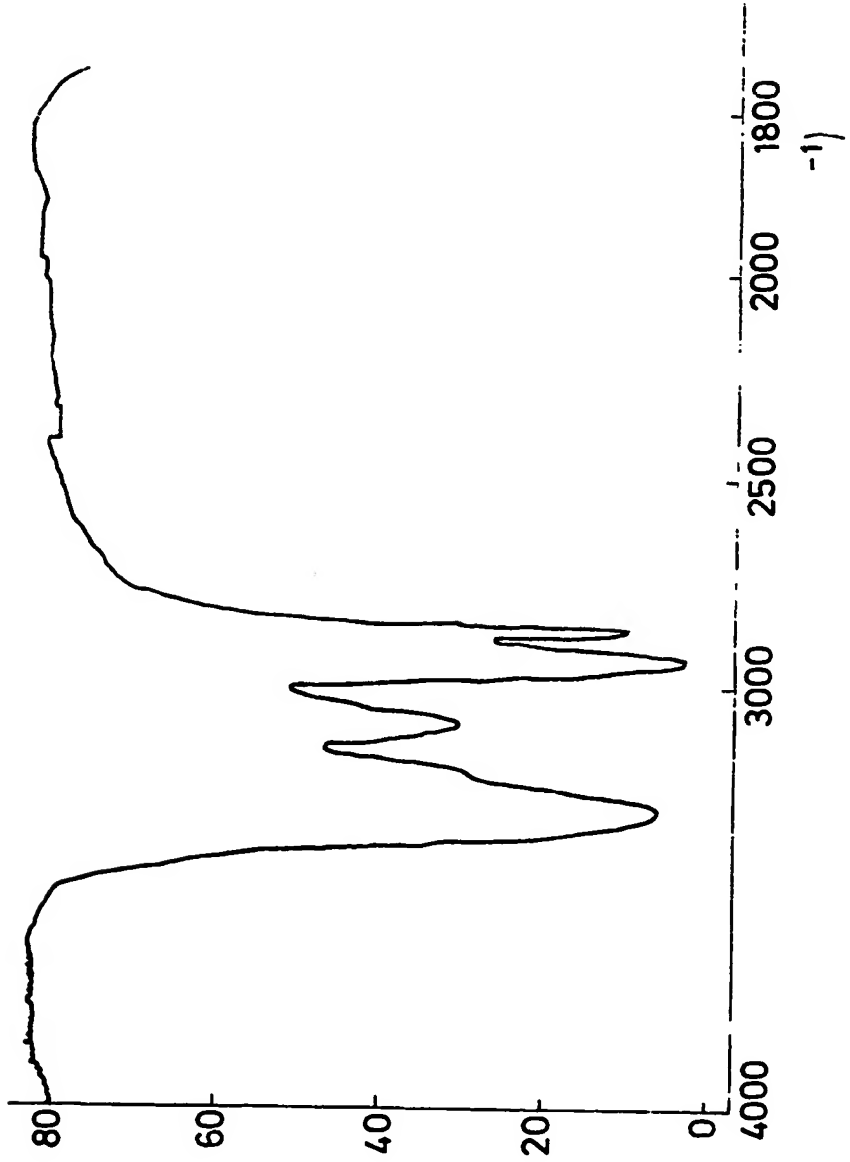
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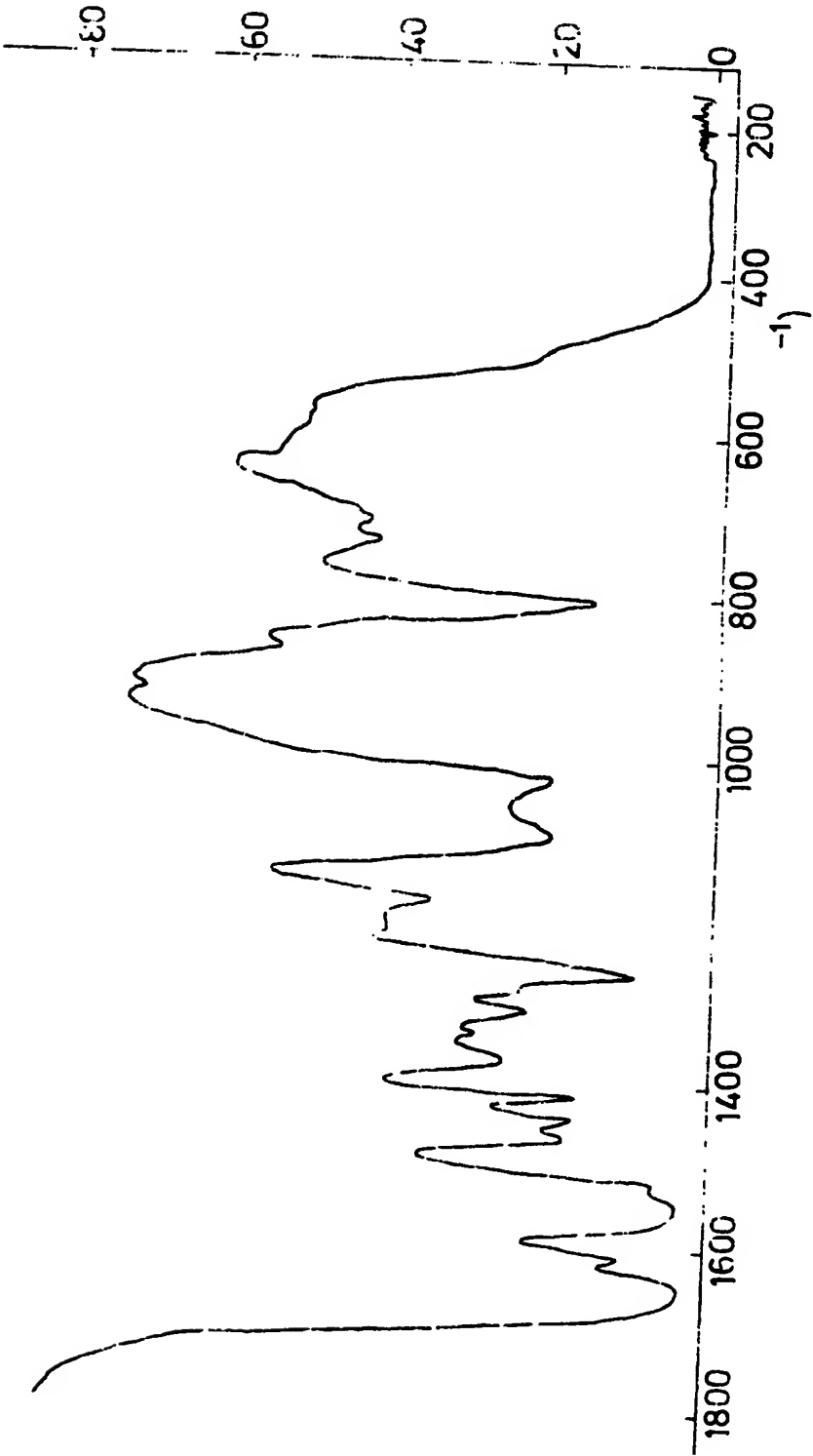
FIG. 10 (1)



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FIG.10 (2)

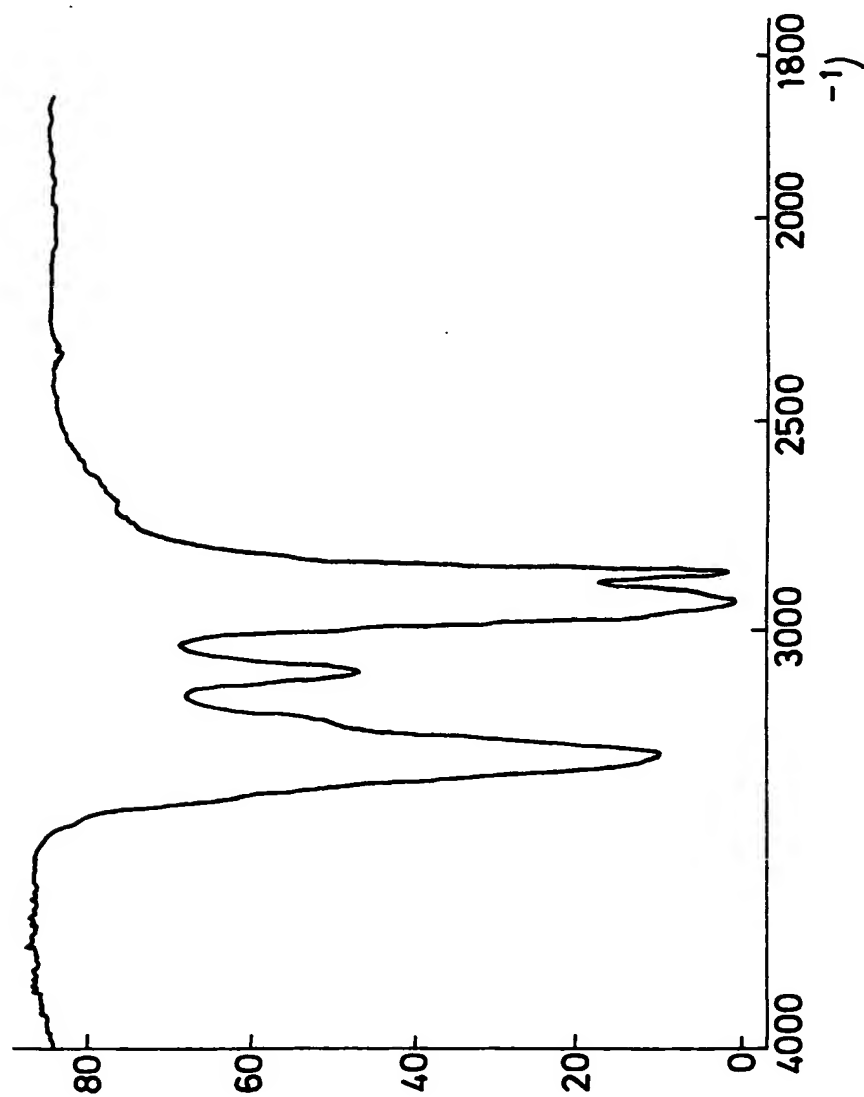




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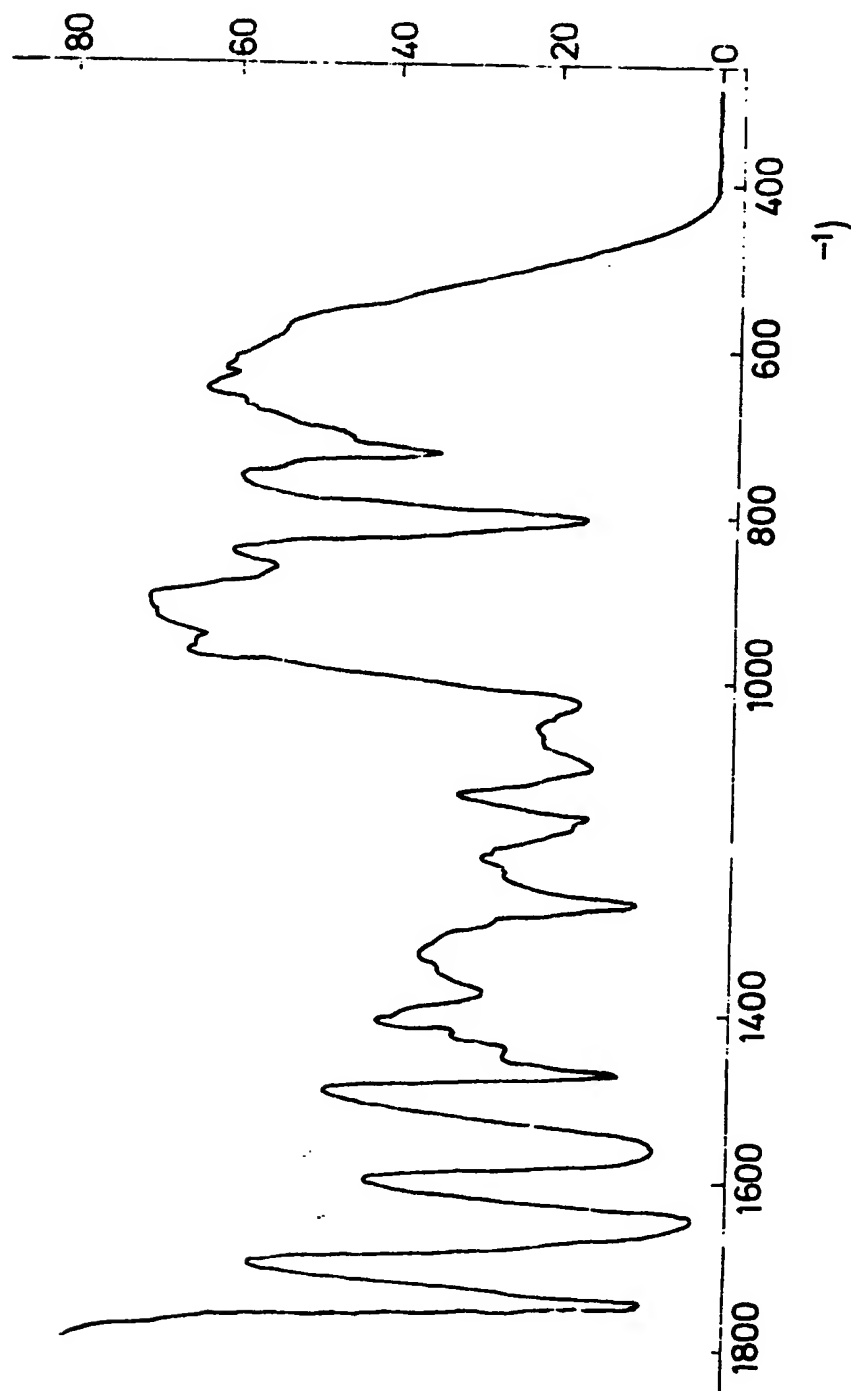
FIG.11 (1)



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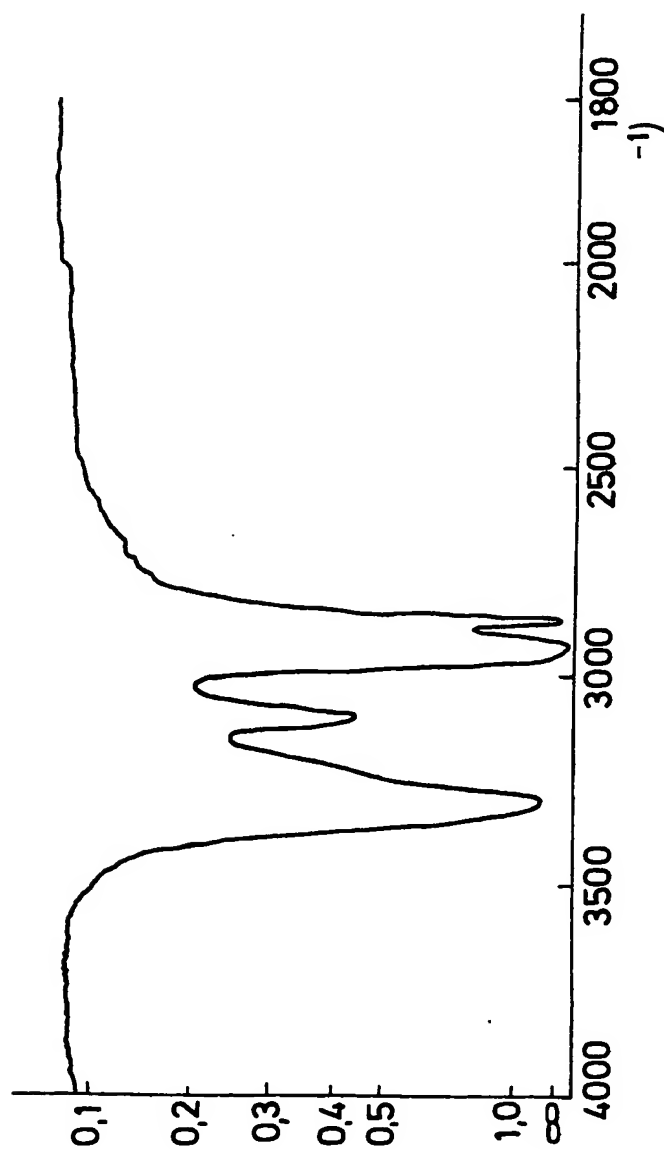
FIG. 11 (2)



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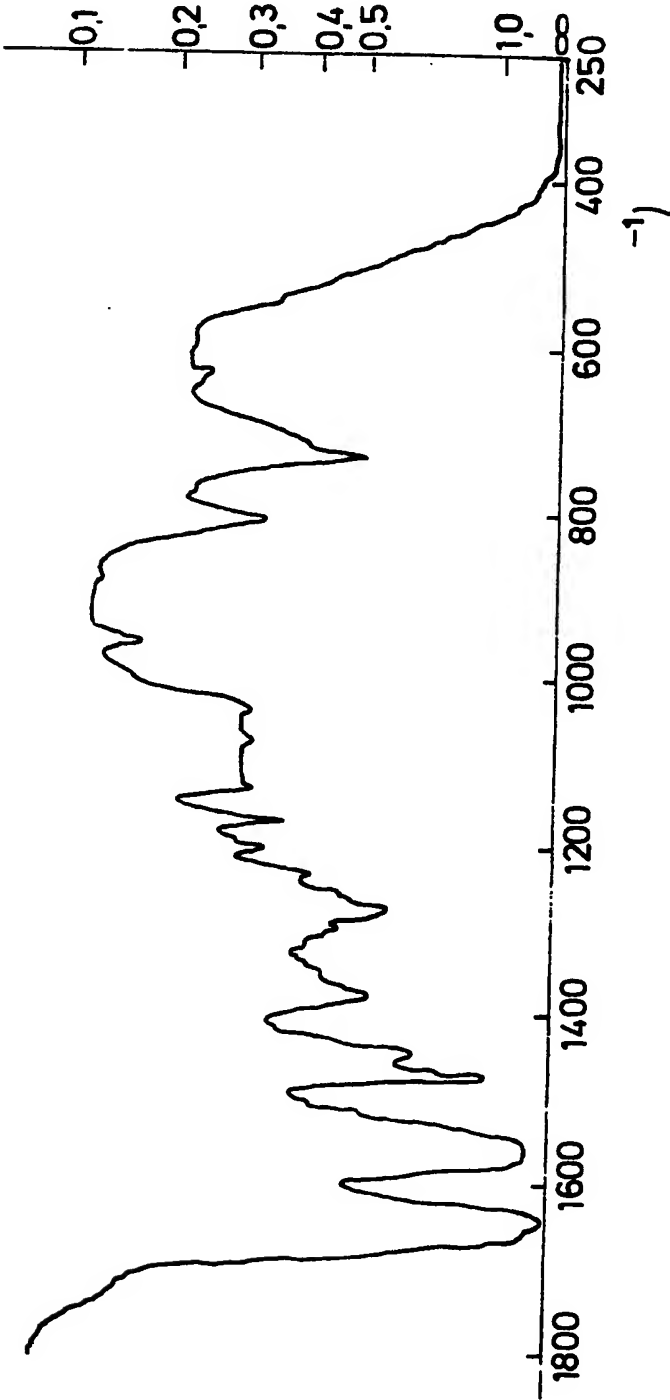
FIG.12(1)



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FIG. 12 (2)



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## SPECIFICATION

## Polyamide-polysiloxane copolymers

- 5 The present invention relates to novel polyamide/polysiloxane copolymers.

Recently, resins or resinous mixtures containing a polysiloxane polymer have attracted interest. It is generally known that polysiloxane polymers have excellent physico-chemical properties such as good resistance to heat and anti-freezing property and are put to practical use as rubbers (silicone rubbers), oils and varnishes, and as various secondary products prepared therefrom. Investigations are now being carried out in many technical fields for increasing the uses of polysiloxane polymers while maintaining the above physico-chemical properties. For example, in the field of engineering plastics, investigations have been carried out to prepare tubes and hoses having a high shock resistance at low temperatures utilizing the elasticity at low temperatures of polysiloxane polymers. In the field of medical supplies, many polysiloxane polymers have been already put to practical use as orthopedic materials, repair materials for blood vessels, and ointment bases utilizing their biochemical stability. Polysiloxane polymers are also used in the field of gas-separating membranes, for such purposes as separation, purification and the like of recycling gases in the purification of helium, separation of rare gases, concentration of uranium, enrichment of oxygen, synthesis of ethanol and synthesis of acetic acid. A membrane for the enrichment of oxygen is already used to give a improved fuel efficiency in boilers.

- 35 Processes for the preparation of resins or resinous mixtures containing a polysiloxane polymer include:

(1) A process of kneading a polysiloxane polymer direct with another resin is described, for example, in Japanese Patent Laid-open No. Sho 58-93749, "Plastics World" page 70, March 1983, etc.  
 (2) A process for the preparation of a block copolymer by chemically bonding a polysiloxane polymer with another polymer such as polyester, polyether, polyurethane, polycarbonate or the like is described, for example, in Ann. N.Y. Acad. Sci., 146, 119 (1967) by W. L. Roff, J. Mom, Sci., 1, by W. J. Ward, USP 3,781,378.  
 (3) A process of graft-copolymerizing a polysiloxane with a suitable trunk polymer is described, for example, in Japanese Patent Laid-open No. Sho 57-135007 and Collected Manuscripts for High Molecular Society 31, 461 (1982).  
 (4) A process for synthesizing high molecules by anionic polymerization of a polymerizing radical containing a polysiloxane as substituent on the side chain is described, for example, in Japanese Patent Publication No. Sho 52-21021.

It is considered that the most suitable process for making resins or resinous mixtures having useful mechanical, electrical and physical properties is process (2) wherein a block copolymer is obtained by

chemically bonding a polysiloxane polymer with another polymer.

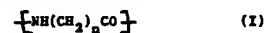
Polyamides are known to have excellent mechanical properties, heat resistance and abrasion resistance, as well as excellent surface appearance. They are widely used for domestic or industrial instruments and apparatus, electronic parts, automobile parts, toothed wheels and the like.

For uses such as soles of shoes, binding belts, inner packing and flexible hoses for automobiles, however, a higher flexibility than that of conventional polyamides is required and there are used polyamide elastomers synthesized from a polyamide and a polyether.

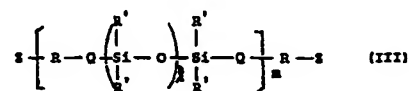
Such polyamide/polyether copolymers, however, lose their useful properties at a low temperature such as from 0°C to 40°C. Also the oil resistance is lowered by their polyether constituent.

It has been found that by bonding a polyamide with a polysiloxane by amide linkage or ester linkage, there may be made a novel polyamide/polysiloxane copolymer having a good heat resistance, water-absorption resilience and chemical resistance, as well as excellent properties usual in polyamide resins such as mechanical properties, abrasion resistance, gasoline resistance and lubricant oil resistance.

According to the present invention, there is provided a polyamide-polysiloxane copolymer comprising a polyamide constituent (A) having repeating units of general formulae (I) and/or (II):



wherein n is an integer from 5 to 11, x is a C<sub>6</sub>—C<sub>12</sub> alkylene radical and Y is a C<sub>4</sub>—C<sub>10</sub> alkylene radical, and amino groups or carboxyl groups at both terminals, and a polyorganosiloxane constituent (B) of general formula (III):



wherein l is an integer from 2 to 50, m is an integer from 1 to 6, Q is an oxygen atom or a direct bond, R' is a hydrogen atom, a methyl group or a phenyl group, R is a divalent organic radical and Z is a hydroxyl group, an amino group or a carboxyl group, the constituents (A) and (B) being polymerized by amide linkages or ester linkages to give a straight chain polyamide copolymer having a J-value of 10—600 ml/g.

The polyamide copolymers of this invention have improved mechanical strength and plasticity at low temperature, hydrolysis resistance, heat resistance, oil resistance, chemical resistance, blood coagulating property compared with conventional polyamide resins or elastomers.

The polyamide copolymers of this invention are useful for separation film, being usable not only at

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy. Formulae in the printed specification were reproduced from drawings submitted after the date of filing, in accordance with Rule 20(14) of the Patents Rules 1982.

ambient temperature but at low or high temperature. They may also be used as hot-melt adhesives, fibres, films and for molding and also as biopolymers.

The invention will be described more particularly in

- 5 Examples set out below, the Examples being illustrated with reference to the accompanying drawings, in which Figures 1-12 are graphs showing IR charts of the polyamide copolymers obtained respectively in Examples 1-12.

- 10 The repeating units of formulae (I) and/or (II) in the polyamide constituent (A) of the copolymers may be formed from various polyamide-forming monomers described below.

- There may be used as the polyamide-forming monomers  $C_6-C_{12}$  w-lactams and  $C_6-C_{12}$  w-aminocarboxylic acids. More particularly the w-lactams may be caprolactam, oenantholactam, decalactam, undecalactam or dodecalactam (lauro-lactam).

- 20 The w-aminocarboxylic acids may be 6-amino caproic acid, 8-amino capric acid, 10-amino decanoic acid, 11-amino undecanoic acid or 12-amino dodecanoic acid.

- As the polyamide-forming monomers forming the repeating units of formula (II), there can be used salts of  $C_6-C_{12}$  diamines with  $C_6-C_{12}$  dicarboxylic acids. More particularly the diamines may be salts of hexamethylene-diamine, undecamethylene-diamine or dodecamethylenediamine, while the acids may be adipic acid, azelaic acid, sebacic acid or dodecane dicarboxylic acid.

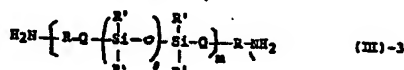
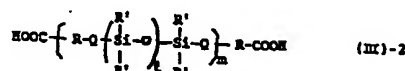
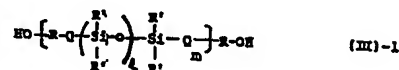
- These polyamide-forming monomers may be used individually or any two or more of them may be used in combination.

- 35 The polyamide constituent (A) should have amino groups or carboxyl groups at both terminals and may be prepared by adjusting the terminals of a polyamide obtained from the above polyamide-forming monomer(s). The adjustment of the terminals is usually carried out by reacting a dicarboxylic acid or diamine with the amino group or the carboxyl group in equivalent amounts. For this purpose various dicarboxylic acids and diamines may be used, examples of which are mentioned hereinafter

- 45 as examples of the third constituent (C). Polyamides having repeating units of formula (II) may also be obtained from the same diamine and dicarboxylic acid which are used for the formation of the polyamides by using either one of them in excess.

- 50 Preferably polyamide constituents (A) are prepared by adjusting the terminals with a  $C_6-C_{12}$  dicarboxylic acid or diamine. As examples, there may be used a diamino terminated polyamide modified with hexamethylenediamine, a dicarboxyl terminated polyamide modified with adipic acid, a dicarboxyl terminated polyamide modified with dodecane dicarboxylic acid, and the like. Such adjustment of the terminals, however, may be effected simultaneously with the copolymerization step, when the amount of

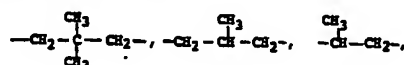
- 60 the dicarboxylic acid or diamine may be controlled to act as a molecular weight adjusting agent. The polyorganosiloxane constituents (B) of formula (III) may be divided into three types, of the following formulae (III)-1, (III)-2, and (III)-3:



- 65 Constituent (B) is selected from these three types such that it may be condensed by amido linkages or ester linkages with the polyamide constituent (A). For example, when a diamino terminated polyamide is used, a dicarboxyl terminated polyorganosiloxane of formula (III)-2 is used (whereby amido linkages are formed). When a dicarboxyl terminated polyamide is used, a dihydroxyl terminated polyorganosiloxane of formula (III)-1 or a diamino terminated polyorganosiloxane of formula (III)-3 is used (whereby ester

- 70 linkages or amido linkages are formed, respectively). In the formula (III), R represents a divalent organic radical which may suitably be an alkylene radical which may be branched, a polyoxyalkylene ( $C_1-C_4$ ) radical having a number average molecular weight of 50-3000, preferably 50-1000, a divalent alicyclic radical or a divalent aromatic radical. As the divalent alicyclic radical a divalent radical containing an alicyclic hydrocarbon group may be used, and as the divalent aromatic radical a divalent radical containing an aryl group may be used.

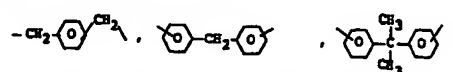
- 85 The preferred alkylene radical is a straight chain or branched  $C_2-C_{36}$  alkylene group. For the branched alkylene group, there may be used for example, groups of the formulae



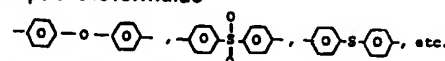
- 90 For the polyoxyalkylene radical, there can be used groups of the formulae  $-(\text{CH}_2\text{CH}_2\text{O})_x-\text{CH}_2\text{CH}_2-$ ,  $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_x-\text{CH}_2\text{CH}_2\text{CH}_2-$ , etc.

- The divalent alicyclic radical may be a group of the formula  $-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-$  or the like,

- 95 which may further be substituted by lower alkyl group(s). Examples of the divalent aromatic radical are groups of the formulae



- which may further be substituted by lower alkyl group(s). The divalent aromatic radical may contain an ether linkage, a sulphonyl linkage, a sulphide linkage or a carbonate linkage, as exemplified by groups of the formulae



- In each of the radicals mentioned above, hydrogen atom(s) may be substituted by halogen atom(s). In formula (III)  $R'$  represents a hydrogen atom, a methyl group or a phenyl group. Although the radicals  $R'$  are usually the same, they can be different. The constituent (B) of formula (III) may comprise a single compound or a mixture. It is preferable to use a

combination of one of low molecular weight (for example  $l=2$  and  $m=1-2$  or  $l=3$  and  $m=1$ ) and one of high molecular weight (for example  $l=5-50$  and  $m=1-6$  or  $l=3-4$  and  $m=2-6$ ). There is a tendency that, as the molecular weight of the organosiloxane moiety in constituent (B) increases, the compatibility of the constituent (B) with constituent (A) decreases and the J-value of the resulting copolymer becomes very low. However, the compatibility is improved and the J-value increases (the resulting copolymer becomes more elastic) by using another constituent (B) having an organosiloxane moiety of low molecular weight. It is believed that the presence of the low molecular weight moiety facilitates free rotation of the main chain of the resulting copolymer. The ratio of low molecular weight constituent to high molecular weight constituent is suitably a molar ratio of 1 : 99—99 : 1, preferably, 10 : 90—90 : 10.

Typical polyorganosiloxane constituents (B) are available under the name "dihydroxy terminated, dicarboxyl terminated or diamino terminated polyorganosiloxane, and modifications thereof".

There are two processes known for the method of polymerization.

1 A process which comprises first preparing a polyamide constituent (A) by polymerization and then copolymerizing (A) with a polyorganosiloxane constituent (B) (two step method).

2 A process which comprises copolymerizing a polyamide-forming monomer for the polyamide constituent (A) with the polyorganosiloxane constituent (B) (one step method).

The polyamide copolymers obtained by the two step method have a polyamide moiety of block type, and the number average molecular weight of their polyamide blocks is suitable 500—50000, preferably, 1000—10000. In contrast, the polyamide copolymers obtained by the one step method have a random polyamide moiety.

In the two steps method, a polyamide constituent (A) is copolymerized with the stoichiometrically equivalent amount of a polyorganosiloxane constituent (B) by ester linkage. The reaction is performed in the presence of an ordinary esterification catalyst at a temperature of about 170—270°C under atmospheric pressure for about 1—4 hours in the

presence of an inert gas, (or 1—6 hr under vacuum). The reaction mixture is then heated at a temperature of 200—270°C under a reduced pressure of 30mmHg or lower, preferably, 10—15mmHg to expedite the polycondensation, and further at a temperature of 220—270°C under a reduced pressure of 1mmHg or lower, preferably, 0.1mmHg or lower. When the copolymerization is performed by amido linkage, the reaction for polycondensation may be carried out at a temperature of about 170—270°C under atmospheric pressure in the presence of an inert gas, in the same manner as described above, but without using any catalyst.

In the one step method, a polyamide-forming monomer is reacted with a dicarboxylic acid or diamine for adjusting the terminals of the polyamide, and a polyorganosiloxane constituent, both in a stoichiometrically equivalent amount, in the manner described above.

As the esterification catalyst there may be used catalyst of the tin series, titanium series and lead series. These may be, for example, dialkyl tin oxides such as dibutyl tin oxide, dioctyl tin oxide; dialkyl tin alkylates such as dibutyl tin laurylate, dibutyl tin bis(2-ethylhexanoate); tetraalkyl titanates such as tetrabutyl titanate, tetraisopropyl titanate, titanium oxalates such as titanium potassium oxalate; lead compounds such as lead acetate. It is preferable to employ tin containing catalysts.

The polyamide copolymers embodying the present invention have a J-value of 10—600, preferably, 20—300. The J-value [ml/g] is an index for evaluating the solution viscosity of a polymer, which is indirectly dependant on the molecular weight of the copolymer. The J-values are determined according to the following method [Deutsche Industrienorm (DIN) 16779 Teil 2]:

In a 50 ml volume measuring flask, 0.25g of a sample is weighted accurately and dissolved in a mixed solvent consisting of phenol/o - dichlorobenzene (1/1) at room temperature or at an elevated temperature.

The volume is adjusted to 50ml. Then, dropping time is measured at 25°C by means of a Ubbelohde viscometer, with respect to the solvent only and to the solution of the sample. J-values are calculated according to the following equation:

$$J\text{-value} = \frac{(\text{dropping time of the solution/dropping time of the solvent only}) - 1}{\text{concentration of the sample (}=0.5\text{g/ml)}} \quad [\text{ml/g}]$$

$$\eta_{\text{rel}} (\text{relative viscosity}) = \frac{\text{dropping time of the solution}}{\text{dropping time of the solvent only.}}$$

The copolymers embodying the present invention comprise substantially a straight chain polymer wherein equivalent amounts of a polyamide constituent (A) and a polyorganosiloxane constituent (B) are connected by amido linkages or ester linkages. The constituent (A) and/or the constituent (B) may be interchanged partially with a third constituent (C) comprising one or more compound of the formula (IV):



wherein J is a hydroxyl group, an amino group or a carboxyl group and R\* is an alkylene radical, optionally branched, a divalent alicyclic radical or a divalent aromatic radical.

The R\* radical may contain one or more hetero atom(s) and its hydrogen atom(s) may be substituted by halogen atom(s).

The third constituent (C) may be used in a ration of 70molar% or less, preferably 1–70molar%, in relation to the polyamide constituent (A), and in a ratio of 99molar% or less, preferably 1–99molar%, in relation to the polyorganosiloxane constituent (B). Advantageously the third constituent is present in a ratio of 3–97molar%, particularly 10–95molar% in relation to constituent (B). The constituent (C) is useful for adjusting the mechanical strength of the copolymer. The third constituent (C) also serves the purpose of making the constituent (A) and the constituent (B) compatible with one another. When the ratio of interchange for constituent (B) exceeds 99molar%, properties of the copolymer resulting from constituent (B) are not obtained. In contrast, when the ratio is less than 1molar%, the compatibility of constituent (B) with constituent (A) on their esterification reaction or amide-forming reaction may be reduced, the molecular weight of the resulting copolymer may be lower and the J-value may be less than 10. When the ratio of interchange with constituent (A) exceeds 70molar%, properties of the copolymer resulting from constituent (A) are not obtained. In contrast, when said ratio is less than 1molar%, the molecular weight of the resulting copolymer may be lower. It is possible partially to interchange both constituent (A) and constituent (B) with a suitable common third constituent (C).

The third constituent (C) may be divided by the functional group into three types having formulae (IV)–1, (IV)–2 and (IV)–3:



Usually, a third constituent (C) having the same functional groups as the constituent (A) or (B) to be interchanged is employed. However, it is also possible to use one having different functional groups. For example, a third constituent (C) of diamine type may be used to replace partially a constituent (B) of diol type, in addition to a third constituent (C) of diol type. A mixture of third constituents (C) of diamine type and diol type may also be used.

Third constituents (C) of formulae (IV)–2 or (IV)–3 may be used for adjusting the terminals of the polyamide constituent (A).

In the formula (IV),  $\text{R}^{\bullet}$  is an alkylene radical, optionally branched, a polyoxyalkylene ( $\text{C}_1-\text{C}_4$ ) radical having a number average molecular weight of 50–3000, preferably 50–1000, a divalent alicyclic radical or a divalent aromatic radical which may contain an ether linkage, a sulphonyl linkage, a sulphide linkage or a carbonate linkage. In each radical, hydrogen atom(s) may be substituted by halogen atom(s). As examples of the radical  $\text{R}^{\bullet}$ , there may be used, for example, the groups illustrated for the radical R in formula (III).

Preferred examples of the third constituent (C) represented by formula (IV)–1 are  $\text{C}_{1-36}$  aliphatic diols such as ethylene glycol, propylene glycol, 1,4-butylene glycol, 1,3-butylene glycol, 1,12-dodecane diol, alicyclic diols such as cyclohexane dimethanol; and polyalkylene glycols having a number average

molecular weight of 50–3000, preferably of 300–3000, such as polypropylene glycol, polytetramethylene glycol or poly-2-methylpropylene glycol.

Preferred examples of dicarboxylic acids of formula (IV)–2 are  $\text{C}_2-\text{C}_{36}$  aliphatic dicarboxylic acids such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, dodecane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, dimer acid, and aromatic dicarboxylic acids such as terephthalic acid or isophthalic acid.

Preferred examples of diamines of formula (IV)–3 are  $\text{C}_6-\text{C}_{36}$  aliphatic diamines such as ethylene diamine, trimethylene diamine, tetra methylene diamine, hexamethylene diamine, undecamethylene diamine, dodecamethylene diamine, dimer diamine (amino compound of a dimer of unsaturated fatty acid such as oleic acid, linolic acid, linolenic acid), 2,2,4,4-trimethyl-hexamethylene diamine; alicyclic diamines such as 1,3/1,4-bis (aminomethyl) cyclohexane, bis (4,4-aminocyclohexyl)methane, isophorone diamine; and aromatic diamines such as xylene diamine or diaminodiphenylmethane.

The ratio by weight of the constituents (A) : (B) : (C) in the copolymers embodying the present invention is preferably 99–1 : 1–99 : 0–30, more particularly, 99–50 : 1–50 : 0–20.

The present invention is further explained hereinafter in the following non-limiting Examples.

#### EXAMPLE 1

In a cylinder type flask of 1l volume were charged: 40g (0.04mol) of dicarboxyl terminated polyamide 12 modified with dodecane dicarboxylic acid ( $\overline{M}_n = 1,000$ ) as constituent (A); 4.3g (0.002mol : 5molar%) of dibutanoloxy terminated polydimethylsiloxane ( $\overline{M}_w = 2,132$ ) as constituent (B); and 3.4g (0.038mol : 95molar%) of 1,4-butane-diol as constituent (C) partially replacing constituent (B). 0.02g of dibutyl tin oxide ( $\text{Bu}_2\text{SnO}$ ) was added as catalyst. The mixture in the flask was heated at 240°C on a metal bath while introducing nitrogen gas and stirred for 2 hours.

Then, the temperature was elevated to 270°C and the stirring was continued for one hour under a reduced pressure (by water jet pump) in the region of 15mmHg. The stirring was continued for another hour under a vacuum of 0.05mmHg (by high vacuum pump) while maintaining the temperature at 270°C. The product obtained, taken out under nitrogen atmosphere, was a white, highly viscous polymer having the following characteristic values. Tg (glass transition temperature) and Tm (melting point) were measured using a DSC (Mettler TA-2000 type or Perkin-Elmer 2C type):

IR: 1745 (ester linkage between polyamide and polydimethylsiloxane and the third constituent), 1260, 1100–1000 and 800  $\text{cm}^{-1}$  (absorptions characteristic of polydimethylsiloxane),  $^1\text{H-NMR}$ : 0.1ppm (signal from the dimethyl group bonded to the silyl group of polydimethylsiloxane), J-value : 81ml/g

Tg : 9°C.  
Tm : 151°C.

From the results of measurement of Torsional vibration, it has been found that there is a second glass transition temperature at 123°C.

Figure 1 shows a chart of the above IR.



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**EXAMPLE 2**

Polymerization was carried out using 20g (0.02mol) of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 1000$ ) as constituent (A), 2.02g (0.002mol : 10molar%) of dibutanoloxy terminated polydimethylsiloxane ( $M_w = 1,005$ ) as constituent (B), 1.62g (0.018mol : 90molar%) of 1,4-butanediol as constituent (C) and 0.01g of dibutyl tin oxide as catalyst, under the same conditions and using the same polymerization apparatus as Example 1.

Characteristic values of the polymer obtained are shown in the following:

IR : 1745 (ester linkage between polyamide and polydimethylsiloxane and the third constituent, 1265, 110-1000 and 800 $\text{cm}^{-1}$  (absorption characteristic of polydimethylsiloxane),  
 $^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),  
 J-value : 78ml/g,

Tg : unclear

Tm : 153°C

Figure 2 shows a chart of the above IR.

**EXAMPLE 3**

Polymerization was carried out using 20g (0.00286mol) of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 7,000$ ) as constituent (A), 1.84g (0.00286mol) of dibutanoloxy terminated polydimethylsiloxane ( $M_w = 645$ ) as constituent (B) and 0.01g of dibutyl tin oxide as catalyst, under the same conditions and using the same polymerization apparatus as Example 1. The polymer obtained had a J-value of 148ml/g, and Tm of 178°C, although its TG was unclear.

Figure 3 shows a chart of IR of the polymer obtained. From the results of measurement of mechanical characteristics by the method of DIN 53455, it was observed that the polymer obtained has a Tensile Modulus of 1402N/mm<sup>2</sup> and Elongation at break of 20%.

**EXAMPLE 4**

Polymerization was carried out using 20g (0.02mol) of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 1,000$ ) as constituent (A), 3.87g (0.006mol : 30 molar%) of dibutanoloxy terminated polydimethylsiloxane ( $M_w = 645$ ) as constituent (B), 1.26g (0.014mol : 70molar%) of 1,4-butanediol as constituent (C) and 0.02g of dibutyl tin oxide as catalyst, under the same conditions and using the same polymerization apparatus as Example 1. The polymer obtained had a J-value of 111ml/g and Tm of 151°C although its Tg was unclear.

Figure 4 shows a chart of IR of the polymer obtained. The polymer obtained has a Tensile Modulus of 245N/mm<sup>2</sup> and Elongation at break of 78%.

**EXAMPLE 5**

Polymerization was carried out using 40g (0.01mol) of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 4,000$ ) as constituent (A), 1.05g (0.0005mol : 5molar%) of didodecanoloxy terminated polydimethylsiloxane ( $N_w = 2,105$ ) as a constituent (B), 0.86g (0.0095 mol : 95molar%) of 1,4-butanediol as constituent (C) and 0.03g of dibutyl tin oxide as catalyst, by means of the same polymerization apparatus and under the same conditions as Example 1.

Characteristic values of the polymer obtained are shown in the following:

IR : 1743 (ester linkage between polyamide 12 and polydimethylsiloxane and 1,4-butanediol, 1275 1100–1000 $\text{cm}^{-1}$  (absorption characteristic of polydimethylsiloxane),

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),

J-value : 79ml/g.

Tg : unclear.

Tm : 172°C.

Figure 5 shows a chart of the above IR.

**EXAMPLE 6**

Polymerization was carried out using 30g (0.03mol) of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 1,000$ ) as constituent (A), 3.52g (0.0015mol : 5molar%) of dipropylamino terminated polydimethylsiloxane ( $M_w = 2,345$ ) as constituent (B) and 4.85g (0.0285mol = 95 molar%) of isophorone diamine as coconstituent (C) and without using any catalyst, under the same conditions and using the same polymerization apparatus as Example 1.

Characteristic values of the polymer obtained were as follows:

IR : 1265, 1100–1000 and 805 $\text{cm}^{-1}$  (absorption characteristic of polydimethylsiloxane),

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),

J-value : 83ml/g

Tg : 37–50°C.

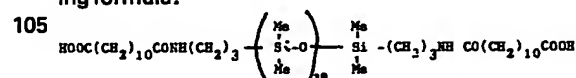
TM : 145°C.

Further, from the results of measurement of Torsional vibration, it has been found that there is a second glass transition temperature at –140°C.

Figure 6 shows a chart of the above IR.

**EXAMPLE 7**

Polymerization was carried out using 24.9g (0.01mol) of diamino terminated polyamide 12 ( $\bar{M}_n = 2,490$ ) as constituent (A), 1.45g (5molar%) of modified polyorganosiloxane ( $M_w = 2,899$ ) of the following formula:



which has been prepared by introducing dodecane dicarboxylic acid residue to both terminals of a diamino terminated polyorganosiloxane ( $M_w = 2,341$ ) as constituent (B) and 2.19g (95molar%) of dodecane dicarboxylic acid as constituent (C) and without using any catalyst, under the same conditions and with the same polymerization apparatus as Example 1.

Characteristic values of the polymer obtained were as follows:

IR : 1260, 1100–1000 and 800 $\text{cm}^{-1}$  (absorption characteristic of polydimethylsiloxane),

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),

J-value : 211ml/g.

Tg : 30–45°C.

Tm : 167°C.

From the results of measurement of Torsional vibration, it has been found that there is a second glass transition temperature at –123°C. The polymer obtained has a Tensile Modulus of 480 N/mm<sup>2</sup> and an Elongation at break of 287%.

Figure 7 shows a chart of the above IR.

**EXAMPLE 8**

Polymerization was carried out using 20g (0.01 mol) of diamino terminated polyamide 11 ( $\bar{M}_n = 2,000$ ) as constituent (A), 1.50g (5molar%) of the modified polydimethylsiloxane ( $M_w = 2,899$ ) used in Example 7 as constituent (B) and 2.19g (95molar%) of dodecane dicarboxylic acid as constituent (C), without any catalyst, under the same conditions and with the same polymerization apparatus as Example 1.

Characteristic values of the polymer obtained were as follows:

IR : 1265, 1100–1000 and 850 $\text{cm}^{-1}$  (absorption characteristic of polydimethylsiloxane),

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),

J-value : 136ml/g.

T<sub>g</sub> : unclear.

T<sub>m</sub> : 177°C.

Figure 3 shows a chart of the above IR.

**EXAMPLE 9**

Polymerization was carried out using 39g (0.03mol) of dicarboxylic terminated polyamide 6 ( $\bar{M}_n = 1,300$ ) modified with adipic acid as constituent (A), 2.16g (0.003mol : 90molar%) of dibutanoloxy terminated polydimethylsiloxane ( $M_w = 719$ ) as constituent (B), 2.43g (0.027mol 10molar%) of 1,4-butanediol as constituent (C) and 0.02g of dibutyl tin oxide as catalyst, using the same polymerization apparatus and under the same conditions as Example 1.

Characteristic value of the polymer obtained were as follows:

$^1\text{H-NMR}$  : 1.1ppm (signal from the dimethyl group bonded to the silyl group),

J-value : 49ml/g.

T<sub>g</sub> : 12–22°C.

T<sub>m</sub> : 186°C.

From these values, it is noted that the polymer obtained is a copolymer of polyamide 6 and polydimethylsiloxane.

Figure 9 shows a chart of an IR carried out on the copolymer.

**EXAMPLE 10**

Polymerization was carried out using 30g (0.03mol) of dicarboxyl terminated polyamide 6 ( $\bar{M}_n = 1,000$ ) as constituent (A), 7.04g (0.003mol : 10molar%) of dipropylamino terminated polydimethylsiloxane ( $M_w = 2,345$ ) as constituent (B) and 5.35g (0.027mol : 90molar%) of diaminodiphenylmethane as constituent (C), using the same polymerization apparatus and under the same conditions as Example 1.

Characteristic values of the polymer obtained were as follows:

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group),

T<sub>g</sub> : 57–65°C.

T<sub>m</sub> : unclear

J-value : 68ml/g.

The polymer obtained has a Tensile Modulus of 709N/mm<sup>2</sup> and an Elongation at break of 39%.

IR chart of the copolymer is shown as Figure 10.

**EXAMPLE 11**

In a cylinder type flask of 1 volume were charged 20g of dicarboxyl terminated polyamide 12 ( $\bar{M}_n = 1,000$ ) as constituent (A), 6.07g (35molar%) of di-2-methylpropanoloxy terminated polydimethylsilox-

ane ( $M_w = 867$ ) and 4.03g (65molar%) of 2-methylpropanoloxy tetramethyl disiloxane ( $M_w = 310$ ) as constituent (B) and 0.02g of dibutyl tin oxide as catalyst. The mixture in the flask was heated at 240°C on a metal bath while introducing nitrogen gas, and stirred for 2 hours. Then the temperature was raised to 270°C and the stirring was continued for 1.5 hours under a reduced pressure (by water jet pump) of about 15mmHg. Under a vacuum of 0.05mmHg (by high vacuum pump) the stirring was continued for a further 2 hours while maintaining the temperature at 270°C. As taken out under nitrogen atmosphere, the product obtained was a white, highly viscous polymer having the following characteristic values:

IR : 1745 (absorption by the ester linkage between organosiloxane and polyamide), 1260, 1100–1000 and 800 $\text{cm}^{-1}$  (absorption by polydimethylsiloxane).

$^1\text{H-NMR}$  : 0.1ppm (signal from the dimethyl group bonded to the silyl group of polydimethylsiloxane),

J-value : 188ml/g.

T<sub>g</sub> : unclear.

T<sub>m</sub> : 149°C

An IR chart of the copolymer produced is illustrated in Figure 11.

**EXAMPLE 12**

In a cylinder type flask of 1l volume were charged 21.96g (90molar%) of diamino terminated polyamide 12 ( $M_w = 2,440$ ) and 10g (100molar%) of dicarboxyl terminated polyamide 12 ( $M_w = 1,000$ ) as constituent (A), and 2.35g (10molar%) of propylamine polydimethylsiloxane ( $M_w = 2,345$ ) as constituent (B). The mixture was heated to 200°C and stirred for 1 hour, while introducing nitrogen gas. The temperature was then raised to 250°C and stirring was continued for 0.5hour under a reduced pressure (by water jet pump). The stirring was continued for 1 hour at 270°C under a high vacuum of 0.01mmHg or less.

The polymer obtained had a J-value of 226ml/g, T<sub>g</sub> of –50°C, T<sub>m</sub> of 168°C, a Tensile Modulus of 614 N/mm<sup>2</sup> and an Elongation at break of 11%. An IR chart is shown on Figure 12.

**EXAMPLE 13**

In a cylinder type flask of 1l volume were charged 20g of dicarboxyl terminated polyamide 12 ( $M_w = 4,000$ ) as constituent (A), 2.27g of dibutanoloxy terminated polydimethylsiloxane as constituent (B), 2.5g of 1,4-butanediol as constituent (C) and 0.01g of dibutyl tin oxide as catalyst. The mixture was heated at 250°C for 2 hours under normal pressure with stirring, while introducing nitrogen gas. The stirring was continued at 250°C for 1 hour under a reduced pressure in the region of 20–30 mmHg (by water jet pump), followed by stirring at 270°C for 2 hours under vacuum of 0.1mmHg (by high vacuum pump) to give the copolymer of the present invention. The copolymer obtained had a J-value of 215ml/g, T<sub>g</sub> of –70°C, and T<sub>m</sub> of 171°C.

In the above Examples 1–13, the number average molecular weight of each polyamide constituent was calculated from the concentration of the amino or carboxyl group on their terminals, according to the following method:

In the case of a terminal carboxyl group, the polyamide constituent was dissolved in warm

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benzyl alcohol and methanol was added to the solution. Titration was then effected with 0.1M KOH/methanol at room temperature.  
In the case of a terminal amino group, titration was

5 effected in a similar manner to that above, at room temperature but with 0.1M HCl/methanol. The method of calculation was as follows:

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$$\text{terminal amino group (eq/g)} = \frac{A \times 0.1 \times F \times 10^{-3}}{W}$$

15

A: amount (ml) of the titrant 0.1N-HCl  
F: factor of 0.1N-HCl  
W: amount (g) of the sample

20

$$\text{terminal carboxyl group (eq/g)} = \frac{(A-B) \times 0.1 \times F \times 10^{-3}}{W}$$

25

Where A: amount (ml) of the titrant 0.1N-KOH  
B: amount (ml) of the titrant 0.1M-KOH at blank  
F: Factor of 1.1N-KOH  
Calculation of mean molecular weight

$$\bar{M} = \frac{2}{[\text{terminal amino group (eq/g)}] + [\text{terminal carboxyl group (eq/g)}]}$$

Table 1

		Example 1		Example 2		Example 3		Example 4	
Polyamide constituent (A)	80th centimol	COOH	wt%	COOH	wt%	COOH	wt%	COOH	wt%
[The general formula (I) and/or the general formula (II)]	Repeating unit	$\text{NH}(\text{CH}_2)_{11}\text{CO}$	83.5	$\text{NH}(\text{CH}_2)_{11}\text{CO}$	84.6	$\text{NH}(\text{CH}_2)_{11}\text{CO}$	81.6	$\text{NH}(\text{CH}_2)_{11}\text{CO}$	79.6
	Mw	1000		1000		7000		1000	
polyorgano-siloxane constituent (B)	l	4 - 6		4 - 6		2		2	
	m	5		2		2		2	
	Q	oxygen		oxygen		oxygen		oxygen	
	Z	OH		OH		OH		OH	
	R'	CH <sub>3</sub>	9.0	CH <sub>3</sub>	8.5	CH <sub>3</sub>	8.4	CH <sub>3</sub>	15.4
[The general formula (III)]	R	-C <sub>4</sub> H <sub>9</sub> -		-C <sub>4</sub> H <sub>9</sub> -		-(CH <sub>2</sub> ) <sub>4</sub> -		-C <sub>4</sub> H <sub>9</sub> -	
	Mw	2132		1005		645		645	
The third constituent (C)	J	OH		OH		-		OH	
	R	-C <sub>4</sub> H <sub>9</sub> -	7.1	-C <sub>4</sub> H <sub>9</sub> -	6.9	-	-	-C <sub>4</sub> H <sub>9</sub> -	5.0
J-value (ml/g) of polyamide copolymer		81		78		148		111	

\*Mw: Number average molecular weight

Table 1 (cont'd)

Polyamide constituent (A)	Both terminal	Example 5		Example 6		Example 7		Example 8	
		COOH	wt%	COOH	wt%	NH <sub>2</sub>	wt%	NH <sub>2</sub>	wt%
[The general formula (I) and/or the general formula (II)]	Repeating unit	$-\text{NH}(\text{CH}_2)_{11}\text{CO}-$	95.4	$-\text{NH}(\text{CH}_2)_{11}\text{CO}-$	78.2	$-\text{NH}(\text{CH}_2)_{11}\text{CO}-$	77.3	$-\text{NH}(\text{CH}_2)_{10}\text{CO}-$	94.5
	M <sub>n</sub>	4000		1000		2420		2000	
polyorgano-siloxane constituent (B)	l	4-6		28		29		29	
	m	2		1		1		1	
	Q	oxygen		direct bond		direct bond		direct bond	
	Z	OH		NH <sub>2</sub>		NH <sub>2</sub>		NH <sub>2</sub>	
	R'	CH <sub>3</sub>	2.5	CH <sub>3</sub>	9.2	CH <sub>3</sub>	7.6	CH <sub>3</sub>	9.2
	R	$-\text{C}_{12}\text{H}_{24}-$		$-\text{C}_3\text{H}_6-$		$-\text{C}_3\text{H}_6-$		$-\text{C}_3\text{H}_6-$	
The third constituent (C)	J	OH		NH <sub>2</sub>		COOH		COOH	
	R''	$-\text{C}_4\text{H}_8-$	2.1	$-\text{C}_4\text{H}_8-$	12.6	$-(\text{CH}_2)_{10}-$	5.1	$-(\text{CH}_2)_{10}-$	6.3
J-value (ml/g) of polyamide copolymer		79		83		211		136	

\*M<sub>n</sub>: Number average molecular weight

Table 1 (cont'd)

Polyamide constituent (A)	Both terminal	Example 9		Example 10		Example 11		Example 12	
		COOH	wt%	COOH	wt%	COOH	wt%	NH <sub>2</sub>	wt%
[The general formula (I) and/or the general formula (II)]	Repeating unit	$-\text{NH}(\text{CH}_2)_9\text{CO}-$	89.4	$-\text{NH}(\text{CH}_2)_5\text{CO}-$	70.8	$-\text{NH}(\text{CH}_2)_{11}\text{CO}-$	66.4	$-\text{NH}(\text{CH}_2)_{11}\text{CO}-$	93.2
	M <sub>n</sub>	1300		1000		1000		2440	1000
polyorgano-siloxane constituent (B)	l	4-6		28		4-6	1	29	
	m	2		1		2	1	1	
	Q	oxygen		direct bond		oxygen	oxygen	direct bond	
	Z	OH		NH <sub>2</sub>		OH	OH	NH <sub>2</sub>	
	R'	CH <sub>3</sub>	5.0	CH <sub>3</sub>	16.6	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	6.8
	R	$-\text{C}_6\text{H}_{12}-$		$-\text{C}_3\text{H}_6-$		$-\text{C}_6\text{H}_{12}-$	$-\text{C}_6\text{H}_{12}-$	$-\text{C}_3\text{H}_6-$	
The third constituent (C)	J	OH		NH <sub>2</sub>		-		-	
	R''	$-\text{C}_4\text{H}_8-$	5.5	$-\text{C}_4\text{H}_8-$	12.6	-		-	
J-value (ml/g) of polyamide copolymer		49		68		188		225	

\*M<sub>n</sub>: Number average molecular weight

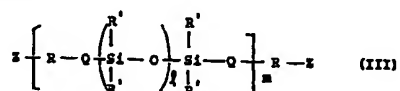
## CLAIMS

1. A polyamide-polysiloxane copolymer comprising a polyamide constituent (A) having repeating units of general formulae (I) and/or (II):

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wherein n is an integer from 5 to 11, X is a C<sub>6</sub>-<sub>12</sub> alkyne radical and Y is a C<sub>4</sub>-C<sub>10</sub> alkyne radical and amino groups or carboxyl groups are both terminals, and a polyorganosiloxane constituent (B) of general formula (III):



wherein l is an integer from 2 to 50, m is an integer

15 from 1 to 6, Q is an oxygen atom or a direct bond, R' is a hydrogen atom, a methyl group or a phenyl group, R is a divalent organic radical and Z is a hydroxyl group, an amino group or a carboxyl group, the constituents (A) and (B) being polymerized by amide 20 linkages or ester linkages to give a straight chain polyamide copolymer having a J-value of 10-600 ml/g.

2. A copolymer as claimed in claim 1, wherein the polyamide constituent (A) comprises a block 25 polyamide moiety having a number average molecular weight of 500-50000.

3. A copolymer as claimed in claim 1, wherein the polyamide constituent (A) comprises a random polyamide moiety.

30 4. A copolymer as claimed in any one of the preceding claims, wherein R is an alkyne radical, optionally branched, a polyalkylene (C<sub>1</sub>-C<sub>4</sub>) radical

having a number average molecular weight of 50–3000, a divalent alicyclic radical or a divalent aromatic radical optionally containing an ether linkage, a sulphonyl linkage, a sulphide linkage or a carbonate linkage.

5. A copolymer as claimed in claim 4, wherein one or more hydrogen atoms in said radicals are substituted by a respective one or more halogen atoms.

6. A copolymer as claimed in any one of the preceding claims, wherein the repeating units of formula (I) are formed by ring cleavage of a C<sub>6</sub>–C<sub>12</sub> w-lactam or by condensation of a C<sub>6</sub>–C<sub>12</sub> w-amino carboxylic acid.

7. A copolymer as claimed in any one of the preceding claims, wherein the repeating units of formula (II) are formed by condensation of C<sub>6</sub>–C<sub>12</sub> diamine with a C<sub>6</sub>–C<sub>16</sub> dicarboxylic acid.

8. A copolymer as claimed in any one of the preceding claims, further comprising a third constituent (C) of formula (IV):



wherein J is a hydroxyl group, an amino group or a carboxyl group and R\* is an alkylene radical optionally branched, a polyoxyalkylene (C1–C4) radical having a number average molecular weight of 50–3000, a divalent alicyclic radical or a divalent aromatic radical optionally containing an ether linkage, a sulphonyl linkage, a sulphide linkage or a carbonate linkage, said third constituent (C) replacing part of either the polyamide constituent (A) in a ratio of 70 molar % or less the polyamide constituent (a) and/or the polyorganosiloxane constituent (B) in a ratio of 99 molar % or less.

9. A copolymer as claimed in claim 8, wherein the ratio of interchange of the third constituent (C) for the polyorganosiloxane constituent (B) is 3–97 molar %.

10. A copolymer as claimed in either claim 8 or claim 9, wherein the ratio of interchange of the third constituent (C) for the polyorganosiloxane constituent (B) is 10–95 molar %.

11. A polyamide-polysiloxane copolymer substantially as described herein with reference to the Examples.

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